

The electronic structure of ζ -BEDT-TTF·PF₆ a comparison of self-consistent field and Hubbard model analyses.¹

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The electronic structure of the organic charge-transfer salt ζ -BEDT-TTF·PF₆ was studied using both density functional and Hartree-Fock theories. The results are in qualitative disagreement with experimental conductivity and optical measurements for the material² which suggest a Mott insulator behavior. We examine the Hubbard model for this system in an attempt to understand both the Mott insulating behavior and the failure of the self-consistent field methods to model it.

Studying the details of a Hubbard dimer model, we find that an important component of the analysis is the inclusion of more valence-bond than ionic character in the ground state wavefunction. The Hartree-Fock treatment includes too much ionic character which destabilizes the result. A spin density wave treatment reduces the ionic character, but also contaminates the wavefunction with terms having the incorrect total spin. It is also interesting to note that the one-electron density and therefore the density functional approach in its usual form is nearly blind to the valence-bond content of the wavefunction.

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[2] H.-L. Liu and co-workers, *Chem. Mater.* **9**, 1865 (1997).